

SELF-HEATING OF CARBONACEOUS MATERIALS

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INTRODUCTION

For quite a few years, Great Lakes Carbon Corporation has produced semi-calcined petroleum coke on a commercial scale. This coke is calcined to a maximum temperature of about 1600°F. For many years previous to this, both raw petroleum coke and fully calcined petroleum coke were handled in quantity and essentially no difficulty was encountered with spontaneous combustion. However, experience has demonstrated that semi-calcined coke is much more liable to spontaneous combustion and special precautions are necessary in handling this material. The present investigation was undertaken in connection with this phenomena.

Because of the importance of spontaneous combustion, particularly with respect to the storage of certain coals and lignites, quite a number of investigations have been conducted. There were a number of investigators who worked early in this century. Among the earliest workers to study the self-heating of coal under adiabatic conditions were Davis and Byrne⁽¹⁾. In their investigation the sample was charged to a vacuum insulated container which was surrounded by an oil bath controlled to follow the temperature of the sample under test. All of their investigations

were conducted using dry coal and dry oxygen. The tests were started at approximately 70°C and usually terminated at about 140°C. They concluded that the heating tendencies of coals high in oxygen are greater in general than those of coals low in oxygen, although the heating tendency is not in all cases proportional to the oxygen content. The heating tendencies of coals of a similar rank are approximately the same. More recent work was done by Heusinger and Muenzner⁽²⁾. In their study tests were made at different starting temperatures with coal of high pyrite content. At >70°C, they found that the heat of oxidation in air gave a temperature rise which would lead to self-ignition in a few days.

In 1928, Rosin⁽³⁾ published a very comprehensive article concerned with spontaneous combustion of semi-coke from brown coal. He pointed out the difference between ignition temperature and liability to spontaneous combustion which are often confused. Ignition temperature is the temperature at which ignition takes place under defined conditions, and is dependent upon the conditions. Liability to spontaneous combustion is a property possessed by a substance of heating spontaneously to the ignition temperature whereupon combustion ensues. A low ignition temperature is not the primary cause of spontaneous combustion. The quantitative work conducted by Rosin required rather large samples of coke - approximately 24 pounds which were held in insulated containers. Rosin recognized the importance of moisture and of humidity control, although it is not clear to what extent humidity was

controlled in the gases passed over the semi-coke. He concluded that moist, semi-coke absorbs more oxygen than dry semi-coke, and that it is more liable to spontaneous combustion. Also, that semi-coke is an activated carbon containing unsaturated compounds which absorb oxygen and that the absorption raises the temperature of the semi-coke to a temperature of dangerous oxidation, which finally results in combustion. Based on the work of others, he concluded the heat of wetting is sufficient to raise the temperature of semi-coke to the temperature of dangerous oxidation.

The use of D. T. A. for classifying coals on the basis of their self-heating characteristics was fully investigated by Banerjee and Chakravorty⁽⁴⁾.

The present paper is concerned with the measurement of the self-heating rates of carbonaceous materials when exposed to a stream of nitrogen, oxygen or CO₂ with controlled humidity.

EXPERIMENTAL WORK

Description of Apparatus

In designing the equipment the objective was to provide simple apparatus sufficiently well insulated so that the rather small heat of absorption or reaction could be followed by the rise in temperature of the carbonaceous material under test. It was desired to accomplish this without the necessity of having the ambient temperature closely follow the temperature rise of the sample, and without the necessity of using a very large sample.

A sketch of the apparatus is shown in Figure 1. It consists of a one-quart, wide mouth Dewar flask in an oven which may be held at constant temperature. The gases, nitrogen, oxygen or carbon dioxide, were supplied from tanks and the flow measured with a rotameter at room temperature. The gas then flowed to a flask filled with water, fitted with an electric heater in which the gas was dispersed by means of a fritted disc and allowed to rise through the water so as to saturate it.

Heat input was automatically controlled by the water temperature. The water saturated gas then flowed through a coil contained within the temperature controlled oven just ahead of the Dewar flask. The temperature of the gas was measured just prior to its entrance into the Dewar flask, using a thermocouple. A thermocouple was also mounted approximately one inch from the bottom of the sample contained in the Dewar flask. The steel tube which supplied the gas stream to the Dewar flask was fitted with a perforated platform at its base which closely fitted the inside diameter of the Dewar flask. The sample was placed on the platform which provided distribution of the gas.

In early tests some difficulty was encountered in obtaining satisfactory Dewar flasks due to insufficient insulation. Prior to placing a Dewar flask in use, its behavior was checked using a standard sample. It was found that heavy walled Pyrex Dewars were best for this particular application, as they provided maximum insulation.

The silvered Dewars used were 70 mm. I. D., 90 mm O. D., 250 mm. deep and contained no separation pads at the base. The evacuation was approximately 1×10^{-7} mm. of mercury.

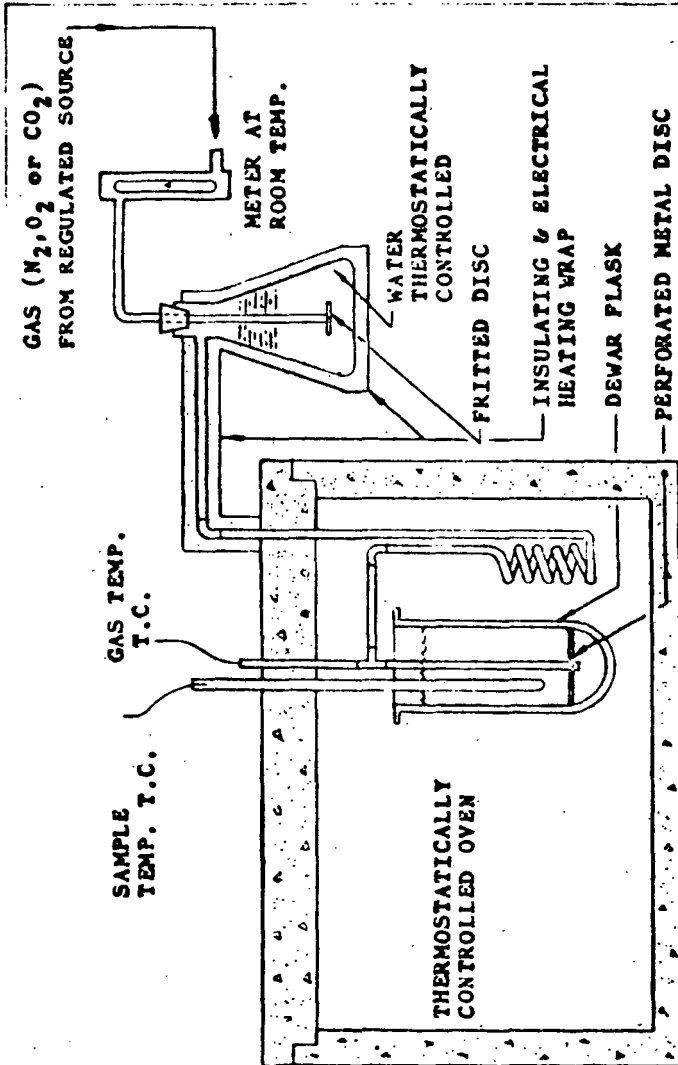


FIG. 1.
APPARATUS FOR SELF-HEATING OF CARBONACEOUS MATERIALS

Sample Preparation

The as-received semi-calcined petroleum coke was carefully crushed to produce a maximum of -3 on 14 mesh particles. In order to standardize test conditions, the majority of the tests were made using coke samples which were air-dried at 220°F. Vacuum drying and drying in an inert atmosphere were investigated. The temperature rise and the shape of the temperature versus time curve were within the limit of reproducibility of the test regardless of the method of drying.

The -3 on 14 mesh size fraction was also used for all other raw materials tested.

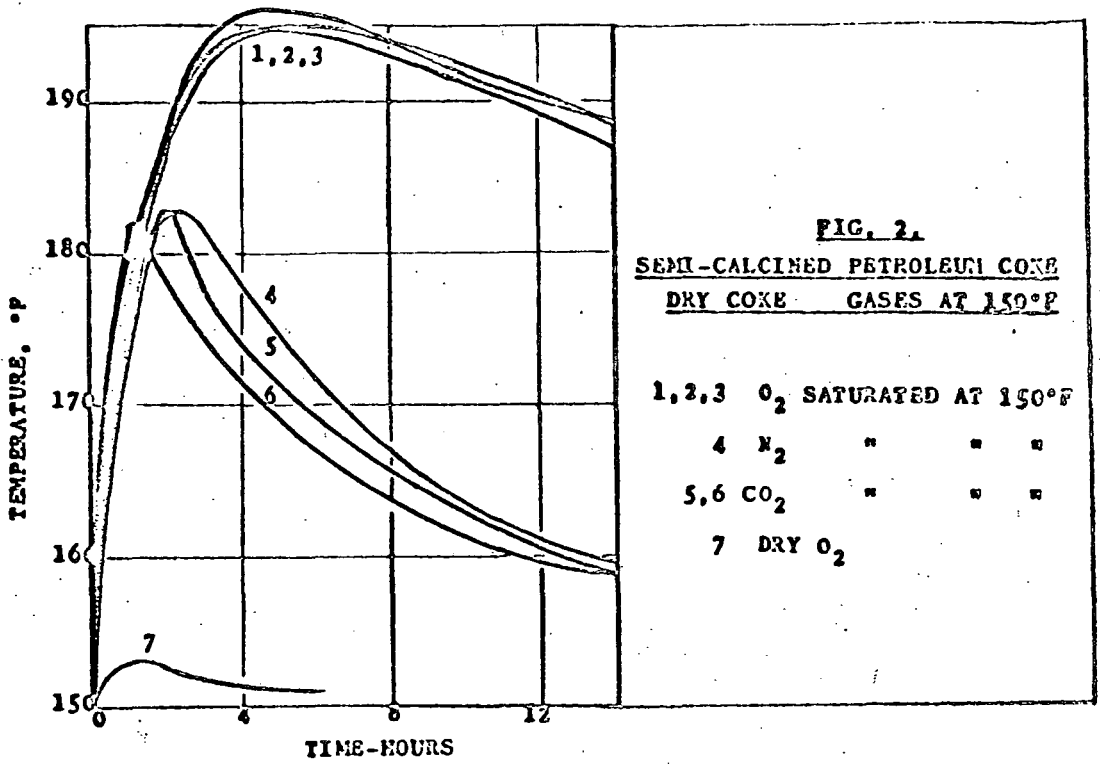
Test Procedure

Due to the extremely low rate of heat transfer between the oven and the sample contained in the Dewar, it was necessary to charge the sample at approximately 150°F. Dried samples at 220°F were allowed to cool to approximately 150°F and then charged to the Dewar. A 600 g. sample was used. The temperature of the sample was then adjusted to 150°F by passing dry nitrogen gas through to either cool or heat the sample. To make certain the system was in equilibrium, it was held for at least ten minutes at 150°F prior to starting a run. The desired gas was then passed through the sample at a controlled flow rate, usually 0.5 cu.ft./hr. and was saturated with water at 150°F, if desired. The furnace temperature, inlet gas temperature, and temperature of the sample at a point one inch above the bottom of the sample were recorded, versus time.

RESULTS AND DISCUSSION

In Figure 2 is shown a graph for a number of runs conducted on a sample of semi-calcined petroleum coke. All runs were made with representative portions of the same sample of coke. Curves 1, 2 and 3 were runs in triplicate made with oxygen, Curve 4 was a run made with nitrogen and Curves 5 and 6 duplicate runs made with CO₂. In all runs the gases were at 150°F and saturated with water vapor. The agreement between duplicate runs is quite good and demonstrates the reproducibility of the test procedure. We may attribute the difference between the temperature versus time relationship of Curves 1, 2 and 3 versus the curves for the runs with nitrogen and CO₂ to the presence of oxygen versus nitrogen or CO₂. There is a definite increase in the maximum temperature obtained of about 12°F when oxygen is used rather than the more inert gases. The shape of the curves after the peak temperature has occurred is of interest. With oxygen there is a tendency for the temperature to be sustained for a longer period of time indicating that the oxygen continues to be absorbed or to react, liberating heat, while with nitrogen or CO₂, after the peak is reached, there is a much sharper decrease in temperature with respect to time. These data indicate that the temperature rise due to absorption of water vapor is about 33°F, while that due to O₂ is about 12°F.

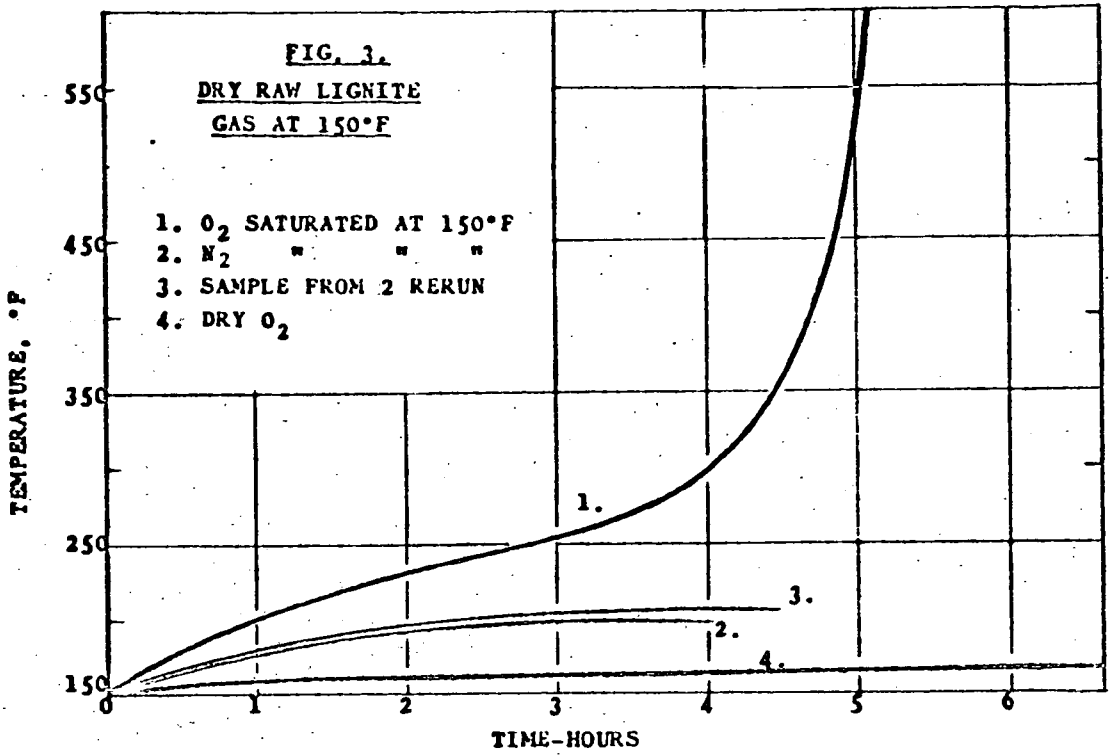
Curve 7 is for a run using dry oxygen at 150°F. The maximum temperature attained was well below that of any of the curves made with saturated gases and indicates that there is little or no reaction or absorption of oxygen in the absence of moisture.

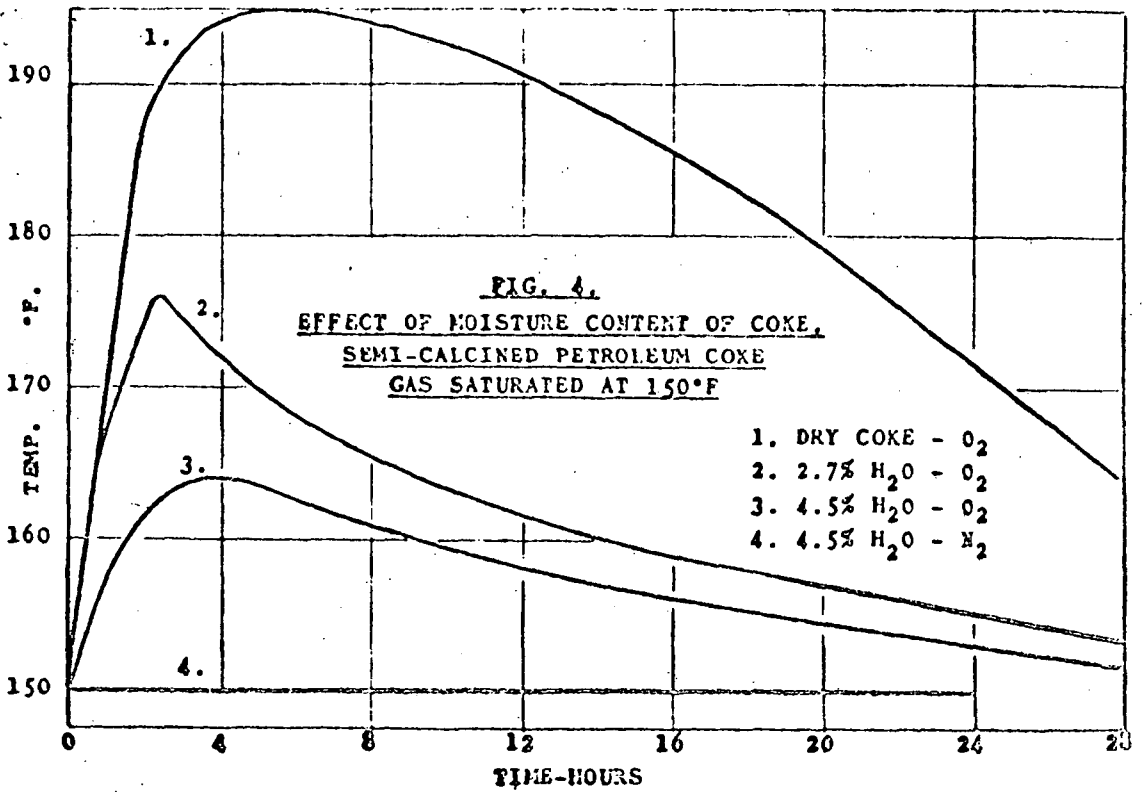


The importance of the role of water in the self-heating of carbonaceous materials is shown more strikingly in Figure 3 in which the sample was dry raw lignite. All runs were made with the gas stream at 150°F. Curve 1 was made with oxygen saturated with water vapor, Curve 2 and 3 with nitrogen saturated with water vapor and Curve 4 with dry oxygen. With dry oxygen the maximum temperature rise was 18°F, with saturated nitrogen 48°F and with saturated oxygen the sample ignited spontaneously in less than 5 hours.

All runs of Figure 4 were conducted using representative portions of a sample of semi-calcined petroleum coke. In runs 1, 2 and 3, the gas was oxygen saturated with water vapor at 150°F; in run 4, it was nitrogen saturated with water vapor. The combination of dry coke exposed to saturated oxygen gave a temperature rise of about 45°F in 5 hours, and as expected, moisture addition to the coke lowered the temperature rise in an atmosphere of saturated oxygen. In run 4 made with saturated nitrogen and coke containing 4.5% water, there was no measurable temperature rise.

From the runs of Figure 2 the contribution of O_2 and water vapor to the temperature rise of semi-calcined petroleum coke was estimated based on the difference between the total rise with saturated O_2 and that with saturated N_2 using dry coke. This amounted to 12°F. In the experiments presented in Figure 4, the coke was saturated with water and the temperature rise due to O_2 measured directly. This amounted to about 14°F,

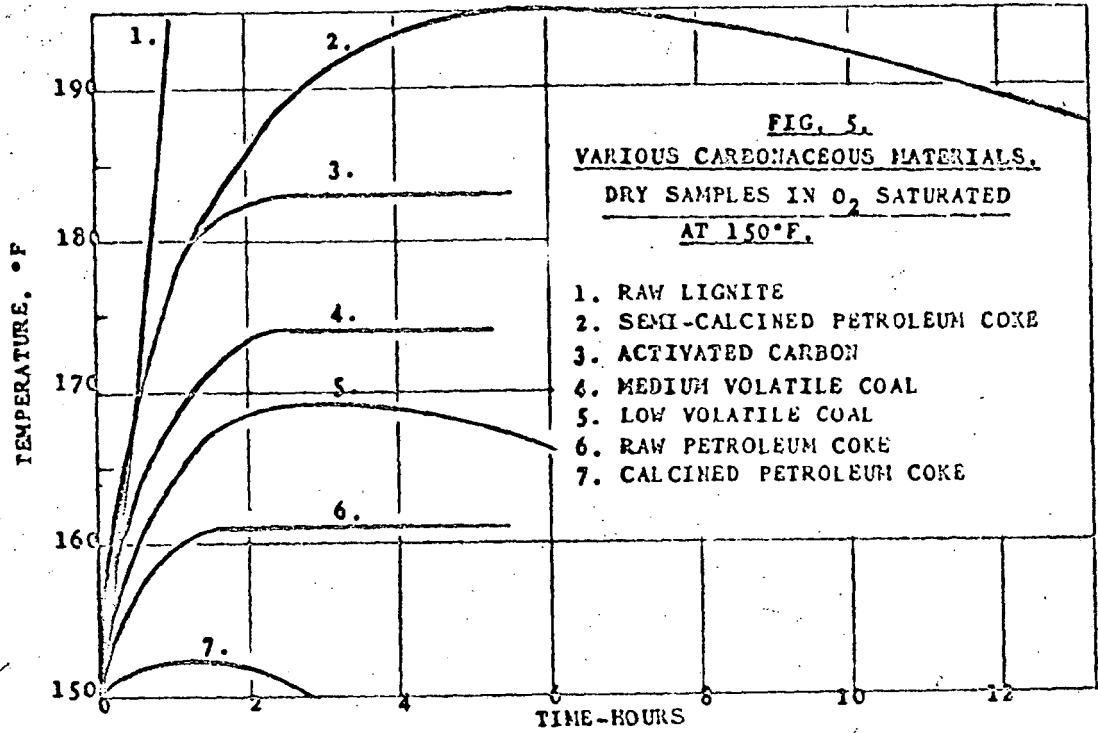




while the rise due to water vapor by difference amounted to 31°F. These are in good agreement with the estimates from Figure 2.

In Figure 5 are shown temperature versus time curves for a variety of carbonaceous materials subjected to a stream of oxygen at 150°F saturated with water vapor. From an examination of the curves it is apparent that lignite, which can be stored with safety only under water, shows the greatest tendency for self-heating in the test apparatus and actually ignites spontaneously in less than five hours. The next most active material is semi-calcined petroleum coke, which shows a maximum temperature rise of about 45°F in five hours. Surprisingly enough this material exhibits a greater temperature rise than a commercial grade of activated carbon which shows a temperature rise of about 33°F. Below this in decreasing order of temperature rise are: a medium volatile (27%) bituminous coal, a low volatile (17%) coal, raw petroleum coke with a volatile matter content of 12%, and finally calcined petroleum coke which exhibits no temperature rise under these conditions. The results of Figure 5 are in good agreement with the known behavior of the various carbonaceous materials upon storage in the field⁽⁵⁾.

The behavior of the activated carbon is of course an exception. Although it exhibits a rather high temperature rise in this test, it is not subject to spontaneous combustion. This is due to the fact that it is well devolatilized and does not contain an appreciable amount of hydrocarbons which are



available for combination with oxygen at temperatures in the range from about 300°F to its ignition point. Thus, it is believed that when this test with oxygen at 150°F saturated with water vapor is applied to materials which are capable of combining with oxygen in the temperature range of 300°F to their ignition temperature, it provides a good measure of the liability of the material to spontaneous ignition.

SUMMARY AND CONCLUSIONS

A simple procedure for the determination of the self-heating rates of various carbonaceous materials has been developed. For those materials which contain sufficient hydrocarbons to combine with oxygen at 300°F and thus ignite at relatively low temperatures, the maximum temperature rise determined in this test correlates with the liability to spontaneous ignition in the field. In a completely dry system there is no serious self-heating evident for any of the materials tested, even in pure oxygen. The absorption of water vapor by the dry carbonaceous material provides the major heating effect in the temperature range from 150°F to about 190°F. This temperature rise will occur even though the moisture be carried by an inert gas such as nitrogen or CO₂. With semi-calcined petroleum coke it has been demonstrated that if oxygen is used, a higher temperature rise of approximately 14°F occurs due to absorption or reaction of the oxygen in the presence of moisture.

The importance of moisture is best illustrated by the behavior of raw lignite which in dry oxygen at 150°F shows a temperature rise of only 18°F in about 5 hours. However, if the oxygen is saturated with water vapor at 150°F, the rate of temperature rise is of the order of tenfold greater, and the lignite ignites in less than 5 hours. Of all of the carbonaceous materials investigated, raw lignite shows the greatest temperature rise in oxygen saturated with water vapor at 150°F. The next most reactive material was semi-calcined petroleum coke which is more active than any of the bituminous coals tested, and in agreement with field experience with this material where considerable difficulty is encountered with spontaneous ignition unless great care is exercised to insure proper cooling prior to storage and to exclude the access of air insofar as possible.

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